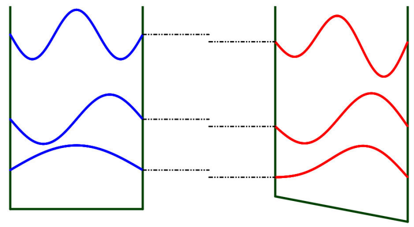

Perturbation Theory

in a nutshell for PHY 444, (updated 2024)

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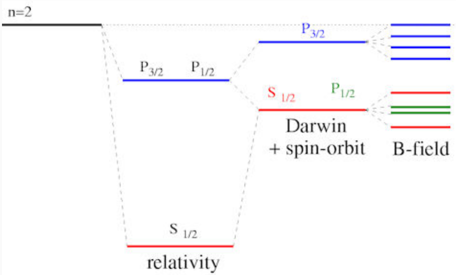
Summary

In perturbation theory, we want to solve the eigenvalue problem

$$\hat{H}|\psi\rangle = E|\psi\rangle, \tag{1}$$

where $\hat{H} = \hat{H}_0 + \lambda\hat{H}_1$.

- We can solve
$$\hat{H}_0|\psi\rangle = E^{(0)}|\psi\rangle. \tag{2}$$
- $\lambda\hat{H}_1$ is a small correction to $\hat{H}_0$.



Perturbation - Algebraic Equation

Consider $x^2 + \epsilon x - 1 = 0$, $|\epsilon| \ll 1$. Exact solution

$$x = -\frac{1}{2}\epsilon \pm \sqrt{1 + \frac{1}{4}\epsilon^2} = \pm 1 - \frac{1}{2}\epsilon \pm \frac{1}{8}\epsilon^2 + \cdots .$$

For $\epsilon = 0$, $x^2 - 1 = 0$ has solution $x = \pm 1$. Seek solution close to $x = 1$.

Assume

$$x(\epsilon) = 1 + \epsilon x_1 + \epsilon^2 x_2 + \cdots .$$

Then,

$$\begin{aligned} 0 &= x^2 + \epsilon x - 1 = 0, \\ &= 1 + 2\epsilon x_1 + \epsilon^2(x_1^2 + 2x_2) + \epsilon + \epsilon^2 x_1 - 1 + O(\epsilon^3). \end{aligned}$$

Coefficient of ϵ : $2x_1 + 1 = 0$. So, $x_1 = -\frac{1}{2}$.

Coefficient of ϵ^2 : $x_1^2 + 2x_2 + x_1 = 0$. Then, $x_2 = \frac{1}{8}$.

This gives solution to order ϵ^3 as

$$x(\epsilon) = 1 - \frac{1}{2}\epsilon + \frac{1}{8}\epsilon^2 + O(\epsilon^3).$$

Perturbation - Eigenvalue Problem

Consider the eigenvalue problem $A\boldsymbol{x} + \epsilon B(\boldsymbol{x}) = \lambda \boldsymbol{x}$.

For $\epsilon = 0$, $A\boldsymbol{x} = \lambda\boldsymbol{x}$ is the unperturbed problem. Assume this is nondegenerate and can be solved for eigenvectors $\boldsymbol{e}$: $A\boldsymbol{e} = a\boldsymbol{e}$.

If A is not symmetric, then the adjoint problem is $\boldsymbol{e}^{\dagger}A = a\boldsymbol{e}^{\dagger}$. Consider the expansions

$$\begin{aligned} \boldsymbol{x}(\epsilon) &= \boldsymbol{e} + \epsilon\boldsymbol{x}_1 + \epsilon^2\boldsymbol{x}_2 \cdots , \\ \lambda(\epsilon) &= a + \epsilon\lambda_1 + \epsilon^2\lambda_2 + \cdots . \end{aligned}$$

Inserting these into the perturbed problem,

$$\begin{aligned} & A\left(\boldsymbol{e} + \epsilon\boldsymbol{x}_1 + \epsilon^2\boldsymbol{x}_2 \cdots\right) + \epsilon B\left(\boldsymbol{e} + \epsilon\boldsymbol{x}_1 + \epsilon^2\boldsymbol{x}_2 \cdots\right) \\ = & \left(a + \epsilon\lambda_1 + \epsilon^2\lambda_2 + \cdots\right)\left(\boldsymbol{e} + \epsilon\boldsymbol{x}_1 + \epsilon^2\boldsymbol{x}_2 \cdots\right). \\ = & a\boldsymbol{e} + \epsilon(a\boldsymbol{x}_1 + \lambda_1\boldsymbol{e}) + \epsilon^2(ax_2 + \lambda_1\boldsymbol{x}_1 + \lambda_1\boldsymbol{e}) + \cdots . \end{aligned}$$

Perturbation - Eigenvalue Problem (cont'd)

At order ϵ^0 : $A\boldsymbol{e} = a\boldsymbol{e}$. This is the unperturbed problem.

At order ϵ^1 : $A\boldsymbol{x}_1 + \epsilon B(\boldsymbol{e}) = a\boldsymbol{x}_1 + \lambda_1\boldsymbol{e}$, or $(A-a)\boldsymbol{x}_1 = \lambda_1\boldsymbol{e} - B(\boldsymbol{e})$,

We need to find λ_1, $\boldsymbol{x}_1$. Multiply by $\boldsymbol{e}^\dagger$. Noting that

$$\boldsymbol{e}^\dagger \cdot (A-a)\boldsymbol{x}_1 = (a-a)\boldsymbol{e}^\dagger \cdot \boldsymbol{x}_1 = 0,$$

we have

$$\boldsymbol{e}^\dagger \cdot (\lambda_1\boldsymbol{e} - B(\boldsymbol{e})) = 0.$$

Solve for λ_1,

$$\lambda_1 = \frac{\boldsymbol{e}^\dagger \cdot B(\boldsymbol{e})}{\boldsymbol{e}^\dagger \cdot \boldsymbol{e}}.$$

Now we can solve for $\boldsymbol{x}_1$:

$$(A-a)\boldsymbol{x}_1 = \frac{\boldsymbol{e}^\dagger \cdot B(\boldsymbol{e})}{\boldsymbol{e}^\dagger \cdot \boldsymbol{e}}\boldsymbol{e} - B(\boldsymbol{e}).$$

Nondegenerate Perturbation Theory

Assume only one eigenstate of $\hat{H}_0$, $|\psi_n^{(0)}\rangle$, with energy $E_n^{(0)}$.

We seek solutions of

$$\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle, \tag{3}$$

in the form

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \ldots, \tag{4}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots. \tag{5}$$

Inserting these into Equation (3),

$$\begin{aligned}\hat{H}|\psi_n\rangle &= \left(\hat{H}_0 + \lambda\hat{H}_1\right)\left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \ldots\right), \\ E_n|\psi_n\rangle &= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots\right)\left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \ldots\right).\end{aligned}$$

Expansions for $\hat{H}|\psi_n\rangle = E_n|\psi_n\rangle$

Expand both sides and equate coefficients of λ^k :

$$\begin{aligned}
\hat{H}|\psi_n\rangle &= \left(\hat{H}_0 + \lambda \hat{H}_1\right)\left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \ldots\right), \\
&= \hat{H}_0|\psi_n^{(0)}\rangle + \lambda\left(\hat{H}_0|\psi_n^{(1)}\rangle + \hat{H}_1|\psi_n^{(0)}\rangle\right) \\
&\quad + \lambda^2\left(\hat{H}_0|\psi_n^{(2)}\rangle + \hat{H}_1|\psi_n^{(1)}\rangle + \hat{H}_2|\psi_n^{(0)}\rangle\right) + \cdots \\
E_n|\psi_n\rangle &= \left(E_n^{(0)} + \lambda E_n^{(1)} + \lambda^2 E_n^{(2)} + \ldots\right)\left(|\psi_n^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \lambda^2|\psi_n^{(2)}\rangle + \ldots\right) \\
&= E_n^{(0)}|\psi_n^{(0)}\rangle + \lambda\left(E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle\right) \\
&\quad + \lambda^2\left(E_n^{(0)}|\psi_n^{(2)}\rangle + E_n^{(1)}|\psi_n^{(1)}\rangle + E_n^{(2)}|\psi_n^{(0)}\rangle\right) + \cdots
\end{aligned}$$

This gives

$$\hat{H}_0|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(0)}\rangle \tag{6}$$

$$\hat{H}_0|\psi_n^{(1)}\rangle + \hat{H}_1|\psi_n^{(0)}\rangle = E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle \tag{7}$$

First Order Energy Shift

Take inner product with basis $\langle\psi_n^{(0)}|$

$$\begin{aligned}\langle\psi_n^{(0)}|\hat{H}_0|\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle &= E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}\langle\psi_n^{(0)}|\psi_n^{(0)}\rangle \\ E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle &= E_n^{(0)}\langle\psi_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}\end{aligned}$$

Then,

$$E_n^{(1)} = \langle\psi_n^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle \tag{8}$$

Take the inner product with basis states $\langle\psi_k^{(0)}|$, $k \neq n$,

$$\begin{aligned}\langle\psi_k^{(0)}|\hat{H}_0|\psi_n^{(1)}\rangle + \langle\psi_k^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle &= E_n^{(0)}\langle\psi_k^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}\langle\psi_k^{(0)}|\psi_n^{(0)}\rangle \\ E_k^{(0)}\langle\psi_k^{(0)}|\psi_n^{(1)}\rangle + \langle\psi_k^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle &= E_n^{(0)}\langle\psi_k^{(0)}|\psi_n^{(1)}\rangle\end{aligned}$$

Therefore, we have the

$$\langle\psi_k^{(0)}|\psi_n^{(1)}\rangle = \frac{\langle\psi_k^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle}{E_n^{(0)} - E_k^{(0)}}, \quad k \neq n.$$

So, we have the first order state $|\psi_n^{(1)}\rangle = \sum_{k\neq n}\langle\psi_k^{(0)}|\psi_n^{(1)}\rangle|\psi_k^{(0)}\rangle$.

Results

We have found the first order corrections as

$$E_n^{(1)} = \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle, \tag{9}$$

$$|\psi_n^{(1)}\rangle = \sum_{k \neq n} \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} |\psi_k^{(0)}\rangle. \tag{10}$$

giving the approximate wavefunctions

$$|\psi_n\rangle = |\psi_n^{(0)}\rangle + \sum_{k \neq n} \frac{\langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle}{E_n^{(0)} - E_k^{(0)}} |\psi_k^{(0)}\rangle + \cdots .$$

Second order in λ gives

$$\langle \psi_k^{(0)} | \left(\hat{H}_0 | \psi_n^{(2)} \rangle + \hat{H}_1 | \psi_n^{(1)} \rangle \right) = \langle \psi_k^{(0)} | \left(E_n^{(0)} | \psi_n^{(2)} \rangle + E_n^{(1)} | \psi_n^{(1)} \rangle + E_n^{(2)} | \psi_n^{(0)} \rangle \right)$$

$$E_n^{(2)} = \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(1)} \rangle = \sum_{k \neq n} \frac{\left| \langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle \right|^2}{E_n^{(0)} - E_k^{(0)}}. \tag{11}$$

Example - Energy Correction to Infinite Square Well

Zeroth Order:

$$\psi_n^{(0)}(x) = \sqrt{\frac{2}{L}} \sin \frac{n\pi x}{L}, \quad E_n^{(0)} = \frac{n^2\pi^2\hbar^2}{2mL^2}$$

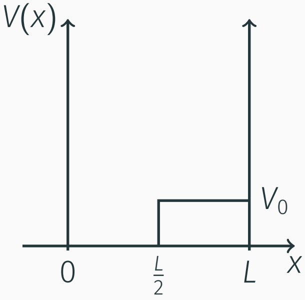


Figure 1: Infinite square well plus perturbation, $V_0 \ll 1$.

First Order:

$$\begin{aligned} E_n^{(1)} &= \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle \\ &= \frac{2}{L} \int_{L/2}^{L} V_0 \sin^2 \frac{n\pi x}{L}\, dx \\ &= \frac{V_0}{L} \int_{L/2}^{L} \left(1 - \cos \frac{2n\pi x}{L}\right) dx \\ &= \frac{V_0}{L} \left[x - \frac{L}{2n\pi} \sin \frac{2n\pi x}{L}\right]_{L/2}^{L} = \frac{V_0}{2}. \end{aligned}$$

Result:

$$E_n \approx \frac{n^2\pi^2\hbar^2}{2mL^2} + \frac{V_0}{2}.$$

The Anharmonic Oscillator

Consider the Hamiltonian

$$\hat{H} = \frac{\hat{p}^2}{2m} + \frac{1}{2}m\omega^2\hat{x}^2 + \lambda\beta\hat{x}^4.$$

Since

$$\hat{x} = \sqrt{\frac{\hbar}{2m\omega}}(\hat{a} + \hat{a}^\dagger),$$

we pick β so that the last term has units of energy. Then,

$$\hat{H}_1 = \frac{\hbar\omega}{4}(\hat{a} + \hat{a}^\dagger)^4,$$

where $\hat{a}|n\rangle = \sqrt{n}|n-1\rangle$, $\hat{a}^\dagger|n\rangle = \sqrt{n+1}|n+1\rangle$, and $[\hat{a}, \hat{a}^\dagger] = 1$.

The unperturbed states are given by $|n\rangle = \frac{(\hat{a}^\dagger)^n}{\sqrt{n!}}|0\rangle$ and the corresponding energies are $E_n^{(0)} = \left(n + \frac{1}{2}\right)\hbar\omega$.

The Anharmonic Oscillator - Energy Corrections

We consider the corrections to the ground state energy, $E_0^{(0)} = \frac{1}{2}\hbar\omega$.

The first order correction is given by $E_0^{(1)} = \frac{\hbar\omega}{4}\langle 0|(\hat{a}+\hat{a}^\dagger)^4|0\rangle$.

We need to compute $(\hat{a}+\hat{a}^\dagger)^4|0>$ as

$$\begin{aligned}
(\hat{a}+\hat{a}^\dagger)^4|0\rangle &= (\hat{a}+\hat{a}^\dagger)^3\left[0+\sqrt{1}|1\rangle\right] \\
&= (\hat{a}+\hat{a}^\dagger)^2\left[\sqrt{1}|0\rangle+\sqrt{2}|2\rangle\right] \\
&= (\hat{a}+\hat{a}^\dagger)\left[\sqrt{2}\sqrt{2}|1\rangle+|1\rangle+\sqrt{2}\sqrt{3}|3\rangle\right] \\
&= (\hat{a}+\hat{a}^\dagger)\left[3|1\rangle+\sqrt{6}|3\rangle\right] \\
&= 3|0\rangle+\sqrt{18}|2\rangle+3\sqrt{2}|2\rangle+\sqrt{24}|4\rangle \\
&= 3|0\rangle+6\sqrt{2}|2\rangle+\sqrt{24}|4\rangle.
\end{aligned}$$

then, we can read off $E_0^{(1)} = \frac{3\hbar\omega}{4}$.

Second Order Ground State Energy Correction

Recall the second order correction:

$$E_n^{(2)} = \langle \psi_n^{(0)} | \hat{H}_1 | \psi_n^{(1)} \rangle = \sum_{k \neq n} \frac{\left| \langle \psi_k^{(0)} | \hat{H}_1 | \psi_n^{(0)} \rangle \right|^2}{E_n^{(0)} - E_k^{(0)}}. \tag{12}$$

So, for harmonic oscillator states, this translates to

$$E_0^{(2)} = \left(\frac{\hbar\omega}{4} \right)^2 \sum_{k \neq 0} \frac{\left| \langle k | \hat{(} \hat{a} + \hat{a}^\dagger)^4 | 0 \rangle \right|^2}{E_0^{(0)} - E_k^{(0)}},$$

where $E_0^{(0)} - E_k^{(0)} = -k\hbar\omega$. Since $(\hat{a} + \hat{a}^\dagger)^4 |0\rangle = 3|0\rangle + 6\sqrt{2}|2\rangle + \sqrt{24}|4\rangle$,

$$E_0^{(2)} = \left(\frac{\hbar\omega}{4} \right)^2 \left[\frac{|6\sqrt{2}|^2}{-2\hbar\omega} + \frac{|\sqrt{24}|^2}{-4\hbar\omega} \right] = -\frac{21}{8}\hbar\omega.$$

This agrees to second order with the results of Bender and Wu [Phys. Rev. 184, 1231, 1969]:[1]
$E_0 = \frac{\hbar\omega}{2} \left(1 + \frac{3}{2}\lambda - \frac{21}{4}\lambda^2 + \frac{333}{8}\lambda^3 - \frac{30855}{64}\lambda^4 + \cdots . \right)$

[1] If $E_0 = \hbar\omega \sum_{n=0}^{\infty} a_n \lambda^n$, then they found $a_n \sim (-1)^{n+1} \frac{\sqrt{6}}{\pi^{3/2}} 3^n \Gamma\left(n + \frac{1}{2}\right)$. The series is factorially divergent!

Appendix - Powers of $\hat{a} + \hat{a}^\dagger$.

We start with a brute force expansion:

$$
\begin{aligned}
(\hat{a}+\hat{a}^\dagger)^2 &= \hat{a}^2 + (\hat{a}^\dagger)^2 + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}. \\
(\hat{a}+\hat{a}^\dagger)^3 &= (\hat{a}+\hat{a}^\dagger)\left[\hat{a}^2 + (\hat{a}^\dagger)^2 + \hat{a}\hat{a}^\dagger + \hat{a}^\dagger\hat{a}\right] \\
&= \hat{a}^3 + \hat{a}(\hat{a}^\dagger)^2 + \hat{a}^2\hat{a}^\dagger + \hat{a}\hat{a}^\dagger\hat{a} + \hat{a}^\dagger\hat{a}^2 + (\hat{a}^\dagger)^3 + \hat{a}^\dagger\hat{a}\hat{a}^\dagger + (\hat{a}^\dagger)^2\hat{a}. \\
(\hat{a}+\hat{a}^\dagger)^4 &= \hat{a}^4 + \hat{a}^2(\hat{a}^\dagger)^2 + \hat{a}^3\hat{a}^\dagger + \hat{a}^2\hat{a}^\dagger\hat{a} + \hat{a}\hat{a}^\dagger\hat{a}^2 + \hat{a}(\hat{a}^\dagger)^3 + \hat{a}\hat{a}^\dagger\hat{a}\hat{a}^\dagger \\
&\quad + \hat{a}(\hat{a}^\dagger)^2\hat{a} + \hat{a}^\dagger\hat{a}^3 + \hat{a}^\dagger\hat{a}(\hat{a}^\dagger)^2 + \hat{a}^\dagger\hat{a}^2\hat{a}^\dagger + \hat{a}^\dagger\hat{a}\hat{a}^\dagger\hat{a} + (\hat{a}^\dagger)^2\hat{a}^2 \\
&\quad + (\hat{a}^\dagger)^4 + (\hat{a}^\dagger)^2\hat{a}\hat{a}^\dagger + (\hat{a}^\dagger)^3\hat{a}.
\end{aligned}
$$

How does this get used to obtain the anharmonic oscillator results?

The form of the perturbation term is found from

$$\beta\hat{x}^4 = \frac{\beta\hbar^2}{4m^2\omega^2}(\hat{a}+\hat{a}^\dagger)^4.$$

Setting

$$\frac{\beta\hbar^2}{4m^2\omega^2} = c\hbar\omega$$

to have energy units. So, $\frac{\beta}{4} = c\frac{m^2\omega^3}{\hbar}$. Picking $c = 1$, $\beta\hat{x}^4 = \frac{1}{4}\hbar\omega(\hat{a}+\hat{a}^\dagger)^4$.

Degenerate Perturbation Theory

For eigenstates $|\psi_{n,i}^{(0)}\rangle$, $i = 1, \ldots .N$, with energy $E_n^{(0)}$, let

$$|\psi_n\rangle = \sum_{i=1}^{N} c_i|\psi_{n,i}^{(0)}\rangle + \lambda|\psi_n^{(1)}\rangle + \ldots, \tag{13}$$

$$E_n = E_n^{(0)} + \lambda E_n^{(1)} + \ldots. \tag{14}$$

Goal: Find the c_i's and first order energy shifts by solving the eigenvalue problem

$$H_1\mathbf{c} = E_n^{(1)}\mathbf{c}, \tag{15}$$

where

$$(H_1)_{ji} = \langle\psi_{n,j}^{(0)}|\hat{H}_1|\psi_{n,i}^{(0)}\rangle.$$

Degenerate Perturbation Theory - Derivation of $H_1\mathbf{c} = E_n^{(1)}\mathbf{c}$

We begin with

$$\begin{aligned} \hat{H}_0|\psi_n^{(0)}\rangle &= E_n^{(0)}|\psi_n^{(0)}\rangle \quad (16) \\ \hat{H}_0|\psi_n^{(1)}\rangle + \hat{H}_1|\psi_n^{(0)}\rangle &= E_n^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}|\psi_n^{(0)}\rangle, \quad (17) \end{aligned}$$

but sum over degenerate states with energy $E_n^{(0)}$:

$$|\psi_n^{(0)}\rangle = \sum_{i=1}^{N} c_i|\psi_{n,i}^{(0)}\rangle.$$

Take inner products with orthonormal basis $\langle\psi_{n,j}^{(0)}|$:

$$\begin{aligned} \langle\psi_{n,j}^{(0)}|\hat{H}_0|\psi_n^{(1)}\rangle + \langle\psi_{n,j}^{(0)}|\hat{H}_1|\psi_n^{(0)}\rangle &= E_n^{(0)}\langle\psi_{n,j}^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}\langle\psi_{n,j}^{(0)}|\psi_n^{(0)}\rangle \\ E_n^{(0)}\langle\psi_{n,j}^{(0)}|\psi_n^{(1)}\rangle + \sum_{i=1}^{N} c_i\langle\psi_{n,j}^{(0)}|\hat{H}_1|\psi_{n,i}^{(0)}\rangle &= E_n^{(0)}\langle\psi_{n,j}^{(0)}|\psi_n^{(1)}\rangle + E_n^{(1)}\sum_{i=1}^{N} c_i\langle\psi_{n,j}^{(0)}|\psi_{n,i}^{(0)}\rangle \\ \sum_{i=1}^{N} c_i\langle\psi_{n,j}^{(0)}|\hat{H}_1|\psi_{n,i}^{(0)}\rangle &= E_n^{(1)}c_j, \quad j = 1, \ldots, N. \end{aligned}$$

Stark Effect - External Electric Field

Apply $\mathbf{E} = E\mathbf{k}$, to hydrogen atom.

$$\hat{H} = \frac{\hat{p}^2}{2\mu} - \frac{e^2}{|\hat{\mathbf{r}}|} + e\hat{\mathbf{r}} \cdot \mathbf{E}$$

Then, $\hat{H}_1 = e|\mathbf{E}|\hat{z}$.

- Ground state, $|1, 0, 0\rangle$, is nondegenerate. $(n = 1)$
- First order correction: $E_1^{(1)} = e|\mathbf{E}|\langle 1, 0, 0|\hat{z}|1, 0, 0\rangle = 0$, due to parity $(-1)^\ell$.
- First excited states, for $n = 2$, are degenerate.
- $n^2 = 4$ states, taken in this order:
  $|2, 0, 0\rangle, \quad |2, 1, 0\rangle, \quad |2, 1, 1\rangle, \quad \text{and} \quad |2, 1, -1\rangle$.

The only nonzero matrix entries are

$$(H_1)_{ji} = \langle \psi^{(0)}_{n,j} | \hat{H}_1 | \psi^{(0)}_{n,i} \rangle.$$

For example,[2]

$$\begin{aligned} \langle 200 | \hat{H}_1 | 210 \rangle &= e|\mathbf{E}| \int_0^\infty r^2\,dr \int_0^\pi \sin\theta\,d\theta \int_0^{2\pi} d\phi R_{20}^* Y_{00}^* r\cos\theta R_{21} Y_{10} \\ &= -3e|\mathbf{E}|a_0. \end{aligned} \tag{18}$$

$$H = \begin{pmatrix} 0 & -\beta & 0 & 0 \\ -\beta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix}, \text{ where } \beta = 3e|\mathbf{E}|a_0. \tag{19}$$

[2] $R_{20} = 2\left(\frac{Z}{2a_0}\right)^{3/2}\left(1 - \frac{Zr}{2a_0}\right)e^{-Zr/2a_0}$, $R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2}\frac{Zr}{a_0}e^{-Zr/2a_0}$,
$Y_{00} = \sqrt{\frac{1}{4\pi}}$, $Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta$, $Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi}$.

Eigenvalue Problem

Solve the eigenvalue problem:

$$\begin{pmatrix} 0 & -\beta & 0 & 0 \\ -\beta & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \\ 0 & 0 & 0 & 0 \end{pmatrix} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} = E_2^{(1)} \begin{pmatrix} c_1 \\ c_2 \\ c_3 \\ c_4 \end{pmatrix} \tag{20}$$

We obtain the energy corrections:

$$\begin{vmatrix} -E_2^{(1)} & -\beta & 0 & 0 \\ -\beta & -E_2^{(1)} & 0 & 0 \\ 0 & 0 & -E_2^{(1)} & 0 \\ 0 & 0 & 0 & -E_2^{(1)} \end{vmatrix} = \left(-E_2^{(1)}\right)^2 \left[\left(E_2^{(1)}\right)^2 - \beta^2\right] = 0,$$

or

$$E_2^{(1)} = 0, 0, \beta, -\beta,$$

and the corresponding eigenvectors,

$$|2,1,1\rangle, |2,1,-1\rangle, \frac{1}{\sqrt{2}}\left(|2,0,0\rangle - |2,1,0\rangle\right), \frac{1}{\sqrt{2}}\left(|2,0,0\rangle + |2,1,0\rangle\right).$$

Matrix elements[3]

$$\begin{aligned}
\langle 200|\hat{z}|210\rangle &= \int_0^\infty r^2\,dr \int_0^\pi \sin\theta\,d\theta \int_0^{2\pi} d\phi R_{20}^* Y_{00}^* r\cos\theta R_{21} Y_{10} \\
&= \frac{2}{4\pi}\left(\frac{a_0}{Z}\right)^4 \left(\frac{Z}{2a_0}\right)^3 \int_0^\infty \rho^4\left(1-\frac{\rho}{2}\right)e^{-\rho}\,d\rho \int_0^\pi \sin\theta\cos^2\theta\,d\theta \int_0^{2\pi} d\phi \\
&= \frac{a_0}{8Z}\left[-\frac{1}{3}\cos^3\theta\right]_0^\pi \int_0^\infty \rho^4\left(1-\frac{\rho}{2}\right)e^{-\rho}\,d\rho \\
&= \frac{a_0}{12Z}\left[4! - \frac{5!}{2}\right] = -\frac{a_0}{12Z}36 = -3a_0. \qquad (21)
\end{aligned}$$

$$\begin{aligned}
\langle 200|\hat{z}|211\rangle &= \int_0^\infty r^2\,dr \int_0^\pi \sin\theta\,d\theta \int_0^{2\pi} d\phi R_{20}^* Y_{00}^* r\cos\theta R_{21} Y_{11} \\
&= \frac{\sqrt{2}}{4\pi}\left(\frac{a_0}{Z}\right)^4 \left(\frac{Z}{2a_0}\right)^3 \int_0^\infty \rho^4\left(1-\frac{\rho}{2}\right)e^{-\rho}\,d\rho \int_0^\pi \sin^2\theta\cos\theta\,d\theta \int_0^{2\pi} d\phi e^{i\phi} \\
&= 0. \qquad (22)
\end{aligned}$$

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[3] $R_{20} = 2\left(\frac{Z}{2a_0}\right)^{3/2}\left(1-\frac{\rho}{2}\right)e^{-\rho/2}, \quad R_{21} = \frac{1}{\sqrt{3}}\left(\frac{Z}{2a_0}\right)^{3/2}\rho e^{-\rho/2}, \quad \rho = \frac{Zr}{a_0}$
$Y_{00} = \sqrt{\frac{1}{4\pi}}, \quad Y_{10} = \sqrt{\frac{3}{4\pi}}\cos\theta, \quad Y_{1,\pm1} = \mp\sqrt{\frac{3}{8\pi}}\sin\theta e^{\pm i\phi},$

Hydrogen Atom Perturbations

Recall the zeroth order energies:

$$E_n^{(0)} = -\frac{\mu c^2 Z^2 \alpha^2}{2n^2}.$$

There are relativistic corrections of order α^4 : the correction to the kinetic energy, spin-orbit coupling, and the Darwin term, given by

$$\hat{H}_K = -\frac{\hat{p}^4}{8m_e^3c^2}, \quad (23)$$

$$\hat{H}_{SO} = \frac{Ze^2}{2m_e^2c^2|\hat{\mathbf{r}}|^3}\hat{\mathbf{L}}\cdot\hat{\mathbf{S}}, \quad (24)$$

$$\hat{H}_D = -\frac{1}{8m_e^2c^2}[\hat{\mathbf{p}}, [\hat{\mathbf{p}}, V(\hat{\mathbf{r}})]]. \quad (25)$$

The relativistic correction to the kinetic energy has rotational invariance, so the degenerate eigenspaces result in diagonal matrix representations for H_1. One only needs to compute

$$E_{n,\ell}^{(1)} = \langle n,\ell,m|\hat{H}_K|n,\ell,m\rangle = -\frac{1}{2}m_e c^2 Z^4 \alpha^4 \left[-\frac{3}{4n^4} + \frac{1}{n^3\left(\ell+\frac{1}{2}\right)}\right]. \quad (26)$$

Spin-Orbit Correction

For this case, the basis states couple position and spin, $|\ell, m, \pm\mathbf{z}\rangle$.

$\hat{H}_{SO}$ commutes with $\hat{J}_z$ and $\hat{\mathbf{J}}^2$.

Eigenvalues of $\hat{J}_z$ equal to $m + \frac{1}{2}$ correspond to the two states $|\ell, m, +\mathbf{z}\rangle$ and $|\ell, m+1, -\mathbf{z}\rangle$ for fixed ℓ and $m \neq \ell$.

The matrix representation for $2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = 2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}} = \hat{L}_+\hat{S}_- + \hat{L}_-\hat{S}_+ + 2\hat{L}_z\hat{S}_z$ is

$$\hbar^2 \begin{pmatrix} m & \sqrt{\ell(\ell+1) - m(m+1)} \\ \sqrt{\ell(\ell+1) - m(m+1)} & -(m+1) \end{pmatrix}. \tag{27}$$

Solving the eigenvalue problem,

$$2\hat{\mathbf{L}} \cdot \hat{\mathbf{S}}|\lambda\rangle = \lambda\hbar^2|\lambda\rangle,$$

one finds $\lambda = \ell, -(\ell+1)$ and the states

$$\begin{aligned} |j = \ell \pm \frac{1}{2}, m_j\rangle &= \sqrt{\frac{\ell \pm m_j + \frac{1}{2}}{2\ell+1}}|\ell, m_j - \frac{1}{2}, +\mathbf{z}\rangle \\ &\pm\sqrt{\frac{\ell \mp m_j + \frac{1}{2}}{2\ell+1}}|\ell, m_j + \frac{1}{2}, +\mathbf{z}\rangle. \end{aligned} \tag{28}$$

Plus the Darwin Term

Eventually, this leads to ($\ell > 0$)

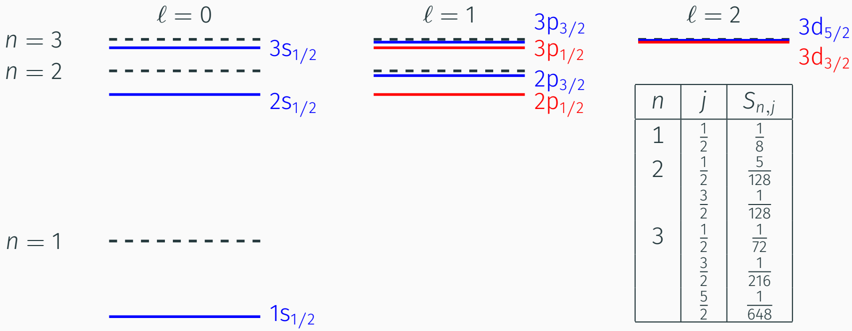
$$E_{SO}^{(1)} = \frac{m_e c^2 Z^4 \alpha^4}{4n^3 \ell(\ell + \frac{1}{2})(\ell + 1)} \begin{cases} \ell, & j = \ell + \frac{1}{2}, \\ -(\ell + 1), & j = \ell - \frac{1}{2}. \end{cases} \tag{29}$$

If $\ell = 0$, there cannot be spin-orbit coupling. But, there is a contribution - the Darwin term. It arises because the electron cannot be confined to a point and must be treated as fuzzy ball.

The final result for the total first order energy corrections:

$$E_{n,j}^{(1)} = -\frac{m_e c^2 (Z\alpha)^4}{2n^3} \left(\frac{1}{j + \frac{1}{2}} - \frac{3}{4n} \right) = -m_e c^2 (Z\alpha)^4 S_{n,j}. \tag{30}$$

Energy Diagram



n	j	$S_{n,j}$
1	$\frac{1}{2}$	$\frac{1}{8}$
2	$\frac{1}{2}$	$\frac{5}{128}$
	$\frac{3}{2}$	$\frac{1}{128}$
3	$\frac{1}{2}$	$\frac{1}{72}$
	$\frac{3}{2}$	$\frac{1}{216}$
	$\frac{5}{2}$	$\frac{1}{648}$

Figure 2: Energy corrections from relativistic perturbation terms. Unperturbed energies at dashed lines.